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Gas–surface interactions with nanocatalysts: Particle size effects in the adsorption dynamics of CO on supported gold clusters

E. Kadossov^a, J. Justin^a, M. Lu^b, D. Rosenmann^c, L.E. Ocola^c, S. Cabrini^d, U. Burghaus^{a,*}^a North Dakota State University, Department of Chemistry and Biochemistry, 202 Ladd Hall, Fargo, ND 58108, USA^b Brookhaven National Laboratory, Center for Functional Nanomaterials, Bldg. 735, Upton, NY 11973, USA^c Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA^d Nanofabrication Facility, Molecular Foundry, LBNL, Berkeley, CA 94720, USA

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ABSTRACT

We present evidence that adsorption probabilities (gas–surface adsorption dynamics) of CO depend distinctly on the Au cluster size, with a reactivity maximum at ~ 3 nm. This cluster size is consistent with the legendary reactivity enhancement seen for the CO-oxidation reaction. Electron beam lithography has been used to fabricate some of the samples (down to 12 nm) as well as physical vapor deposition.

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Bulk gold has been regarded as chemically inert for a long time. However, more recent work [1–4] (see [Supplementary material](#) for more references) shows its remarkable catalytic activity at the nanometer size range. The reasons are still not entirely understood [3,5,6]. Furthermore, the way particle sizes affect gas–surface interactions, which are the first elementary steps in any surface reaction, has rarely been studied in detail [7,8]. This fact is related to experimental difficulties, since a complex ultra-high vacuum (UHV) molecular beam scattering system is required to directly gather information about adsorption dynamics (gas–surface energy transfer processes).

CO is historically used as a probe molecule in surface chemistry studies [9]. In addition, CO-oxidation – one of the most important prototype reactions – strongly depends on the size of the Au clusters [1,5,6,10]. An enhancement in the CO₂ product formation rates, depending on particle size and support, has been reported [1–3].

In this Letter, we present evidence for distinct particle size effects on CO adsorption dynamics by employing molecular beam scattering techniques. The silica supported gold nanoclusters were fabricated by electron beam lithography and physical vapor deposition. In addition, particle size distributions and densities have been carefully analyzed utilizing high-resolution (~ 1 nm) electron microscopy. Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) data have been collected as well.

The initial reactivity of gold nanoclusters towards the adsorption of CO has been characterized by molecular beam scattering. This so-called initial (CO coverage $\rightarrow 0$) adsorption probability, S_0 , is shown as a function of Au deposition time, χ , in [Fig. 1A](#) (solid

squares, left hand scale, thick blue line).¹ Several independent experimental runs have been averaged. Here Au was deposited at 300 K on a UHV cleaned silica support by means of an electron beam metal evaporator. CO was dosed at a surface temperature of 100 K by the molecular beam system. Remarkably, a distinct increase in the reactivity of CO adsorption is evident (see the peak at $\chi \sim 10$ s in [Fig. 1A](#)). This enhancement in catalytic activity correlates with CO TDS data (open spheres, right hand scale, thin orange line in [Fig. 1A](#)). The integrated intensity of CO TDS curves is shown here, which quantifies the total amount of adsorbed CO. For the TDS experiments, the surface has always been saturated with CO using the molecular beam scattering system. Please note that CO does not adsorb with significant concentration on the bare support at the chosen measuring conditions. Similarly, surface temperatures as low as 67 K are required to adsorb CO on terrace sites of Au single crystals [11] (see [Supplementary material](#) for more references and data, see e.g. [Fig. 4A-sup](#)) [Fig. 1B](#) depicts a scanning electron microscopy (SEM) image of a sample morphology corresponding to the maximum in the S_0 vs. χ curve (indicated by the solid red arrow). Finally, [Fig. 1C](#) shows the Au cluster size distribution of this image, in which the Au cluster density amounts to $5 \times 10^{11}/\text{cm}^2$. The particle size distribution is narrow and centered at about 3 nm, consistent with prior scanning tunneling microscopy (STM) studies [12,13].

It is well established that terrace sites on Au surfaces are catalytically inactive; low-coordinated step and kink sites, however, play a major role in gold chemistry [3,14]. According to prior STM studies, the Au growth on silica occurs as seen for most model catalysts (metal-on-metal oxide/semiconductor systems) [12,13].

* Corresponding author. Fax: +1 701 231 8831.

E-mail address: uwe.burghaus@ndsu.edu (U. Burghaus).¹ For interpretation of color in [Fig. 1](#), the reader is referred to the web version of this article.

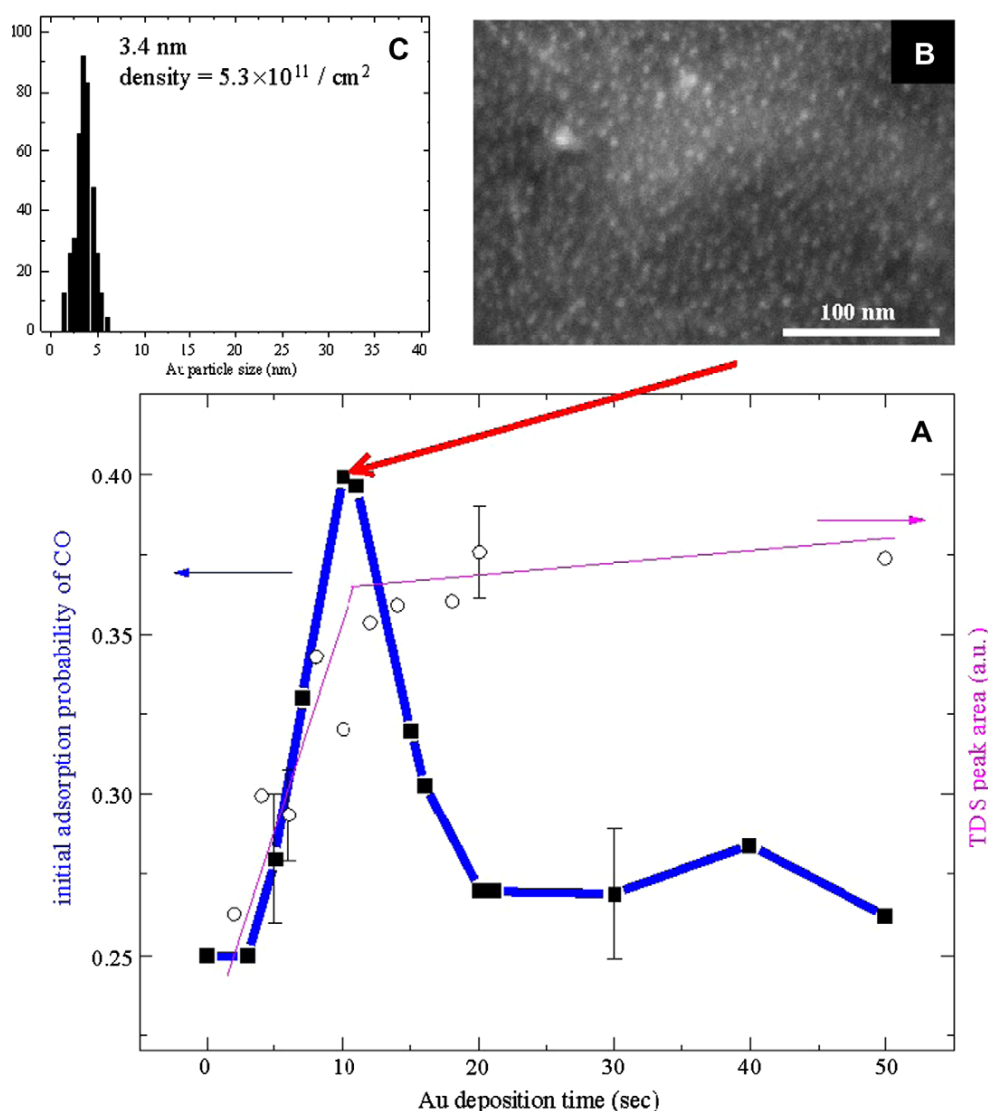


Fig. 1. (A) (squares) Initial adsorption probability, S_0 , vs. Au deposition time, χ (circles) TDS peak area vs. χ (the sample has always been saturated with CO). (B) SEM image for $\chi = 10$ s. (C) Statistical analysis of SEM image (cluster number vs. cluster size in nm).

At small Au coverages, Θ , a quasi-two-dimensional growth mode is present, while very large exposures lead to three-dimensional Au cluster growth. More specifically for silica, the initial particle growth mode consists of two steps [12,13]. During the first step, at the nucleation stage ($\chi < 10$ s), the cluster density increases rapidly with χ . Thus, an increase in the Au coverage corresponds mostly to a raise in the density of small clusters. Therefore, S_0 (see the thick blue line in Fig. 1A) increases proportionally to the increase in the cluster density: The more catalytically active sites are present, the larger S_0 . $S_0(\chi)$ increases initially by 40% or by 0.15 ± 0.04 , see Fig. 1A. We start with no Au clusters on the support (clean surface) and increase the number of clusters while keeping their size relatively unchanged (nucleation phase). Therefore, also the integrated CO TDS intensity initially increases (see the open spheres in Fig. 1A).

During the second step, depositing more gold after nucleation, leads to an increase in the cluster size while keeping the particle density essentially constant [12,13]. Since large Au clusters are less reactive than small ones, a decrease in S_0 would be expected for

large χ , as is indeed observed ($\chi > 10$ s in Fig. 1A). In fact, small Au clusters have a larger fraction of active (low-coordinated) sites than large clusters [15]. However, the total amount of adsorption sites (both terrace and defects) is proportional to the particle surface area and increases with increasing cluster size. Therefore, in nanometer range the CO TDS intensity increases upon dosing more gold in accordance with TDS data from other groups [3,14]. Afterwards, the CO TDS intensity reaches saturation since at large cluster sizes the decrease in relative fraction of low-coordinated sites starts to dominate over the increase in the total number of adsorption sites. Please note that the total amount of Au deposited amounts to less than 1 ML (equivalent Au coverage). Thus, we do not form thick Au films.

Fully consistent with the enhancement in S_0 for ~ 3 nm particles (described above in Fig. 1A) are sintering effects, which become evident when collecting S_0 data as a function of annealing temperature. Interestingly, S_0 decreases with increasing annealing temperature (Fig. 2A). An SEM image of an annealed sample is depicted in Fig. 2B. The statistical analysis (see Fig. 2C) indeed

reveals the formation of much larger clusters (up to 40 nm) and a decrease in the cluster density (to $2 \times 10^{11}/\text{cm}^2$). Thus, small clusters agglomerate to form large clusters (sintering). Furthermore, the value of S_0 for strongly annealed samples agrees with the value obtained for large Au deposition times (large clusters). As the annealing temperature increases, the particle size increases (Fig. 2B and C), the cluster density decreases, and S_0 decreases (Fig. 2A). In addition, the annealing temperature at which S_0 drops (~ 600 K, Fig. 2A) is close to the Tammann temperature of gold (668 K), consistent with the conclusion drawn here.

Samples fabricated by electron beam lithography (known as model nano array catalysts [16,17]) have also been studied. The inset of Fig. 2A depicts a typical SEM for a model nano array catalyst. For 12 nm particles (pitch 100 nm), S_0 agrees with the data obtained for strongly annealed (vapor deposited) Au clusters. However, no CO adsorption was evident for 50 nm clusters. This independently confirms that small Au clusters correspond to large

S_0 values. To the best of our knowledge, the model nano array catalyst samples studied here consist of the smallest cluster size reported so far in a catalysis study (see [Supplementary material](#) for more data).

An enhancement in the CO adsorption dynamics has, in principle, important implications for surface reactions [18]. For example, considering the CO-oxidation reaction, the CO concentration, $[\text{CO}]$, on the catalyst surface is given by $d[\text{CO}]/dt = S_0F - k_d[\text{CO}] - k_r[\text{CO}][\text{O}]$, with k_d and k_r representing the desorption and reaction rate coefficients, respectively. Thus, an increase in S_0 increases the effective CO flux, S_0F , on the surface and therefore $[\text{CO}]$. Hence, the CO_2 product formation rate, $R_{\text{CO}_2} = k_r[\text{CO}][\text{O}]$, increases with S_0 . (F is the CO flux and $[\text{O}]$ the oxygen coverage.) Despite the simplicity of this schematics, the maximum value observed for S_0 , which corresponds to ~ 3 nm Au particles (Fig. 1A), would generate a maximum in $R_{\text{CO}_2}(\chi)$, in agreement with the reactivity enhancement seen in catalysis studies. Certainly many factors affect the

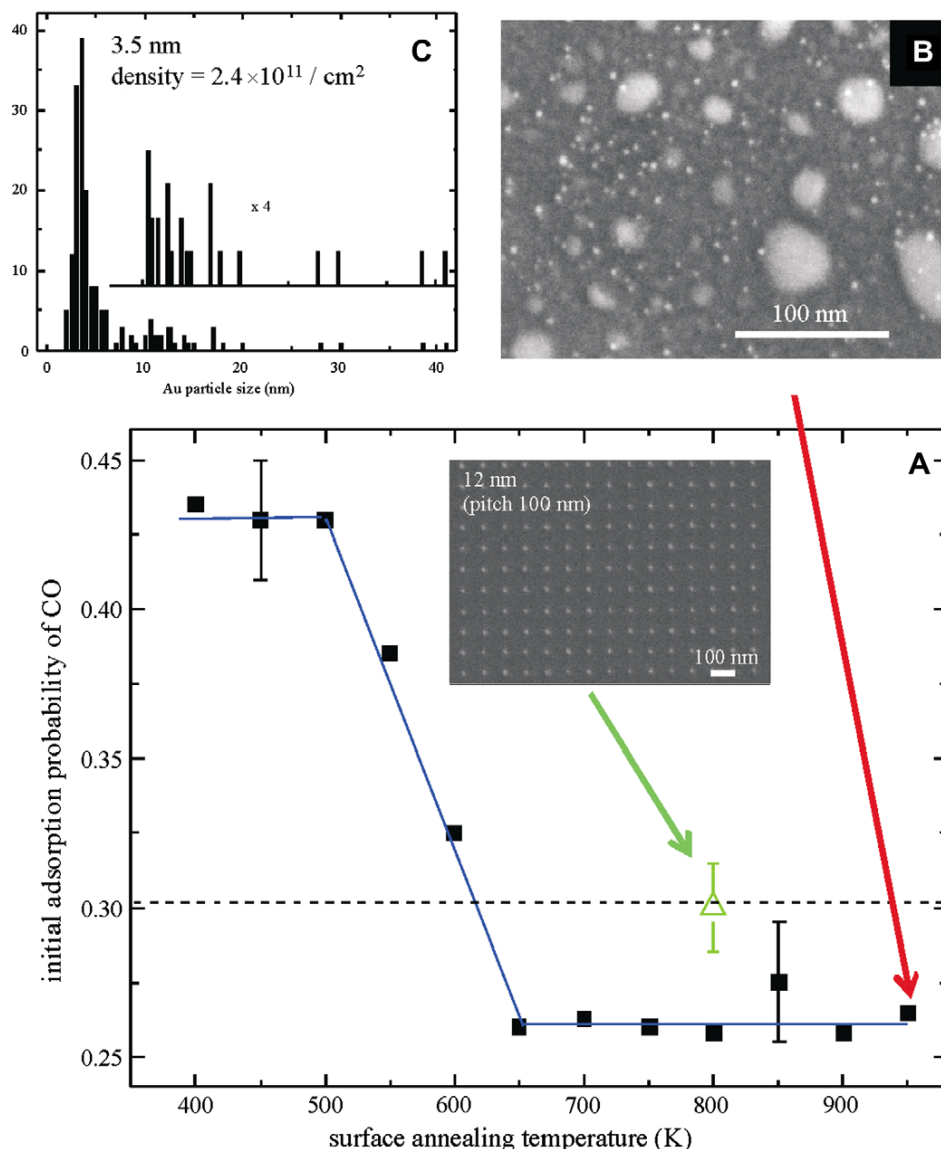


Fig. 2. (A) (squares) S_0 vs. annealing temperature (for $\chi = 10$ s) (inset) SEM of model nano array catalyst and (triangle) corresponding S_0 . (B) SEM image of sample step-wise annealed up to 950 K for 10 s each. (C) Statistical analysis of SEM image shown in panel (B).

reactivity of nanogold, but the adsorption dynamics has so far mostly been overlooked in microkinetics models for nanogold. The simple rate equation model used here to illustrate the effect of the adsorption dynamics on the reaction kinetics does not explicitly include e.g. a possible activation of oxygen or cooperative effects. However, more complicated kinetics would in the simple framework used here solely result in apparent reaction rate coefficient and this would not change qualitatively the conclusions drawn.

In summary, we presented evidence that the gas–surface energy transfer processes governing the reactivity for CO adsorption are strongly affected by the Au cluster morphology (size and dispersion). This effect will in principle also affect surface reactions with CO such as the CO-oxidation reaction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2009.10.083](https://doi.org/10.1016/j.cplett.2009.10.083).

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